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14. ABSTRACT The Air Force has an interest in operating some electronic satellite components at very low temperatures, about 40 K. Novel approaches are presently being pursued with the aim of using solid-state cooling to reach such temperatures. Laser cooling and electroluminescent cooling of solids, for example, are being investigated in other programs as phenomena that may be suitable for new refrigeration technologies. An alternative cooling technology, which sees widespread current application in systems that operate near room temperature, is thermoelectric cooling. This AFOSR research program was focused on the discovery and development of new bulk materials whose thermoelectric properties at low temperature may allow them to ultimately yield appropriate coolers for these low temperature applications. Several new bulk materials systems were identified that might be useful for low temperature cooling applications with further development. One in particular, calcium doped bismuth selenide, shows anomalously good thermoelectric properties at temperatures near 10 Kelvin.					
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Project:

Thermoelectric Materials for Low Temperature Cooling

FA9550-06-1-0530

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Final Project Report

Period covered: August 1, 2006 – August 31, 2009

Thermoelectric Materials for Low Temperature Cooling

1. Objectives:

The Air Force is interested in operating some of its electronic satellite components at very low temperatures, about 40 K. One possible technology for cooling these components is thermoelectric cooling, which is currently widely commercialized in cooling systems that operate near ambient temperature. This AFOSR research program is focused on the discovery and development of new materials whose thermoelectric properties at low temperature may allow them to ultimately yield efficient coolers for these low temperature applications.

2. Summary:

The optimization of thermoelectric materials for low temperature cooling applications involves the optimization and balance of three different materials parameters. These parameters are the electrical resistivity, which should be as small as possible, the Seebeck coefficient, a measure of the heat carried by transported electrical charge, which should be as large as possible, and the thermal conductivity, which should be as small as possible so that the heat transported by the charge does not “leak” back in the other direction. These parameters are temperature dependent, and small band gap semiconductors are optimal for use at low temperatures. A cooling device requires coupled *n*-type and *p*-type cooling legs with similar thermoelectric characteristics in order to function optimally. In this research program, a study of thermoelectric materials based on the Bi-Sb semiconducting alloy system was completed. The optimum *n*-type and *p*-type materials for use in the 50K temperature range were determined through testing different Bi-Sb ratios, and testing the influence of Sn as a *p*-type dopant. These materials were found to be excellent from a mechanical and chemical viewpoint, being highly chemically and mechanically robust, with reproducible properties. However it was concluded that they are not efficient enough to be employed as a basis for a new, low temperature cooling technology. The testing of a second group of materials, based on chemical alteration of the low bandgap semiconductor TiSe_2 , was completed to test a new hypothesis for factors that might yield high quality low temperature thermoelectrics. It was found to be inferior to the Bi-Sb alloy. The low temperature properties of a little-studied family of compounds, $\text{Bi}_2\text{Te}_2\text{S} - \text{Sb}_2\text{Te}_2\text{S}$, related to one of the best room temperature thermoelectrics, Bi_2Te_3 , was also tested. These have very good low temperature thermoelectric properties, suggesting that optimization in future work may be possible. One of the new systems studied, Ca-doped Bi_2Se_3 , has highly anomalous and superior thermoelectric properties at very low temperatures and should be pursued as a potential practical low temperature thermoelectric bulk material for cooling applications. The discovery and initial characterization of this material was performed during this research program.

3. Publications:

“Structures and thermoelectric properties of the infinitely adaptive series $(\text{Bi}_2)_m(\text{Bi}_2\text{Te}_3)_n$ ”, J.W.G. Bos, H.W. Zandbergen, M.H. Lee, N.P. Ong, and R.J. Cava, *Phys. Rev.* **B75** 195203 (2007).

“Synthesis, crystal structure and thermoelectric properties of $\text{IrSn}_{1.5}\text{Te}_{1.5}$ -based skutterudites”, J.W.G. Bos and R.J. Cava, *Sol. St. Comm.* **141** 38 (2007).

“Magnetic and thermoelectric properties of layered $\text{Li}_x\text{Na}_y\text{CoO}_2$ ”, J.W.G. Bos, J.T. Hertz, E. Morosan, and R.J. Cava, *J. Sol. St. Chem.* **180** 3211 (2007).

“*p*-type Bi_2Se_3 for topological insulator and low-temperature thermoelectric applications”, Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J.G. Checkelsky, A. Yazdani, M.Z. Hasan, N.P. Ong, and R.J. Cava, *Phys Rev.* **B79** 195208 (2009).

“Thermoelectric properties of Sn-doped Bi-Sb”, Y.S. Hor and R.J. Cava, *J. Alloys and Compounds* **479** 368 (2009).

“The low temperature thermoelectric properties of $\text{Cu}_x\text{TiSe}_{2-y}\text{S}_y$ ”, Y.S. Hor and R.J. Cava, *Mat. Res. Bull.* **44** 1375 (2009).

“Temperature Dependent Thermoelectric Properties of the $\text{Bi}_2\text{Te}_2\text{S} - \text{Sb}_2\text{Te}_2\text{S}$ Solid Solution”, D. C. Grauer, Y. S. Hor and R. J. Cava, *Mat. Res. Bull.* **44** 1926 (2009).

4. Accomplishments/New Findings:

Bi-Sb The elements Bi and Sb form a continuous single-phase alloy (a solid solution) for all fractional mixtures. Both elements are semimetals, with bands at different wavevectors in the Brillion zone overlapping in

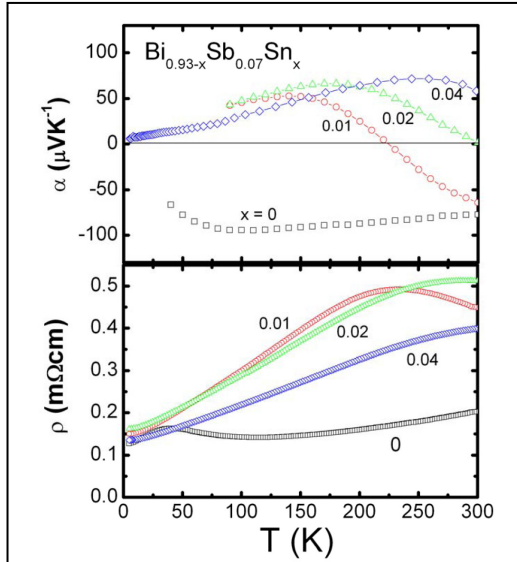


Fig. 1. Upper panel: the Seebeck coefficient from 5 to 300K for Sn-doped $\text{Bi}_{0.93}\text{Sb}_{0.07}$. Lower panel: Temperature dependence of the resistivity for Sn-doped $\text{Bi}_{0.93}\text{Sb}_{0.07}$ between 4 and 300K.

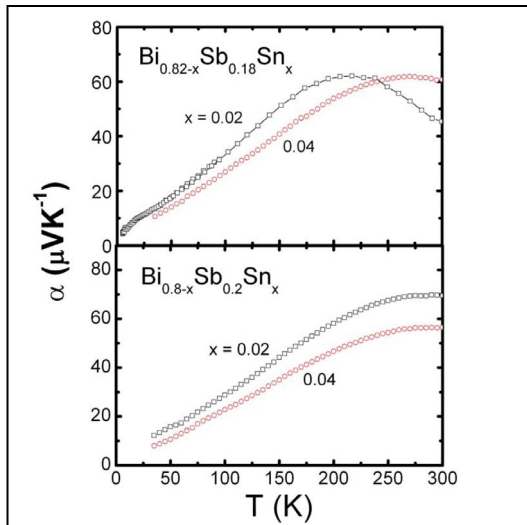


Fig. 2. Upper panel: the Seebeck coefficient from 5 to 300K for Sn-doped $\text{Bi}_{0.82}\text{Sb}_{0.18}$. Lower panel: the Seebeck coefficient from 5 to 300K for Sn-doped $\text{Bi}_{0.8}\text{Sb}_{0.2}$.

create semiconducting behavior, and also to *p*-type dope the alloy, yielding a resistivity behavior more like what is seen for the other compositions.

Figure 2 summarizes the Seebeck coefficients for the Sn-doped alloys at the high Sb limit of the semiconducting region in the Bi-Sb phase diagram. In this composition range, the Seebeck coefficients are positive over the whole temperature range below 300 K even at 2 % Sn doping, and are generally largest for the 2 % samples. The difference between the higher Sb content alloys and the lower Sb content alloys is to move the peak in the positive Seebeck coefficient closer to 300K, but the overall behavior of these *p*-type

mixtures. Both elements are semimetals, with bands at different wavevectors in the Brillion zone overlapping in energy at the Fermi level. In Sb, the origins of those bands are different from what they are in Bi. The result is an unexpected set of band crossings as a function of *x* in the $\text{Bi}_{1-x}\text{Sb}_x$ alloy system. For $\text{Bi}_{1-x}\text{Sb}_x$ at $x=0.07$ the conduction and valence bands touch exactly at the Fermi level, yielding what has been theoretically been predicted to be a “Dirac point”: the energy vs. wavevector dispersions of the bands are expected to be linear rather than parabolic. For the composition region between $x=0.07$ and $x=0.22$ the system is a very small band gap semiconductor. The best thermoelectric materials at low temperatures are expected to be those where the band gaps are very small, at the low *x* part of this composition range and the high *x* part of this composition range. It has been known for some time that the $\text{Bi}_{1-x}\text{Sb}_x$ alloy near $x=0.1$ is an excellent *n*-type thermoelectric. This was worked out in the 1970s and 1980s, but little work has been done on this system since then.

The upper panel of Figure 1 shows the temperature dependent Seebeck coefficient measured for the 7% Sb alloy, near the first opening of the band gap on Sb solution in Bi, for Sn doping levels in the 1–4 % range. The same general behavior is displayed for all materials in this Sb content range. The host Bi-Sb alloys are *n*-type thermoelectrics with Seebeck coefficients in the -75 to $-175 \mu\text{VK}^{-1}$. The substitution of 1 % Sn induces a crossover from *n*-type to *p*-type thermoelectric behavior on cooling to below about 250 – 200K. 2 % Sn substitution raises the *n* to *p* crossover temperature to near room temperature. The maximum Seebeck coefficient displayed is in the range of $+50$ to $+80 \mu\text{VK}^{-1}$, peaking near 200K, depending on the Bi to Sb ratio in the original alloy. The differences in behavior for the Bi-Sb alloys in the range 7-10 % Sb when *p*-doped with Sn at the 4 % level are relatively small. Higher Sn content alloys do not display improved Seebeck coefficients.

The lower panel of Figure 1 shows the behavior of the temperature dependent electrical resistivities below room temperature for the low Sb region. The Sn doping of the 7 % Sb alloy appears both to open the band gap, to

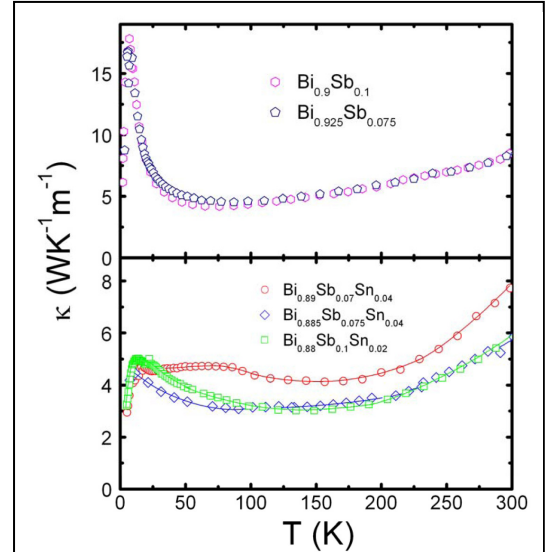


Fig. 3. Temperature dependence of the total thermal conductivities for different Bi-Sb-Sn alloys in the lower Sb-content range. Lower panel, total thermal conductivity for Sn-doped *p*-type alloys, upper panel, total thermal conductivities for host *n*-type alloys.

alloys is quite similar to those at the lower Sb end of the semiconducting region in the phase diagram.

The total thermal conductivities for temperatures below 300K for the alloys at lower Sb contents are presented in figure 3. The upper panel shows the thermal conductivities of undoped Bi-Sb alloys. The thermal conductivities are high compared to the best thermoelectrics such as Bi_2Te_3 . It is surprising that the thermal conductivities increase dramatically at low temperatures in the Bi-Sb alloys, an indication that the phonon mean free path grows significantly with decreasing temperature. This implies that either the thermal conductivity is very insensitive to the mass-disorder scattering that must be present due to the doped Sb, or that there must be short range ordering in the binary alloy system that makes the crystalline perfection much better than what is expected for a random alloy. The lower panel of the figure, which shows the thermal conductivity of the Sn-doped Bi-Sb alloys, shows a behavior exactly like what is expected from a disordered alloy system, where the lack of a peak at low temperatures indicates a structural disorder-induced limitation of phonon mean free path. The figure shows that as little as 2 % Sn doping greatly suppresses the increasing low temperature thermal conductivity seen in the Bi-Sb binary alloy. Since from a mass difference perspective, doping Bi with Sb or Sn is essentially equivalent, this result implies that the small amounts of Sn doping either disrupt any hypothetical short range order present, or introduce dramatic structural defects not otherwise present, e.g. if the doped Sn is interstitial rather than substitutional in the binary alloy. The relatively high thermal conductivities observed, even for the Sn-doped alloys at low temperatures, are a generic problem in this system for attaining high performance low temperature thermoelectrics, and a significant decrease in the thermal conductivity will be needed to achieve competitive thermoelectric efficiencies for this materials family.

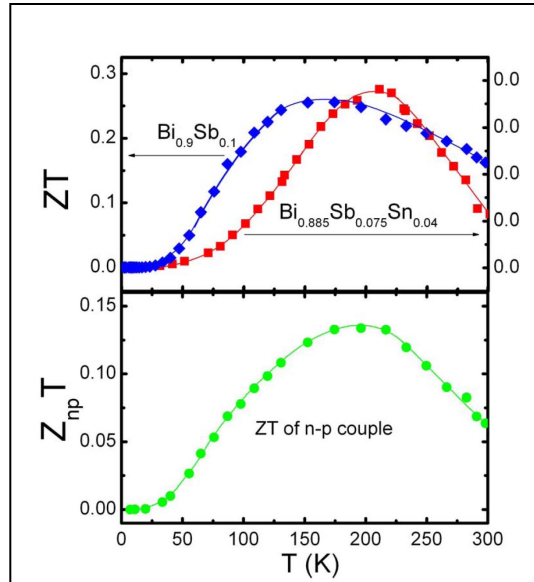


Fig. 4. Upper panel: Thermoelectric figure of merit for the best *n*-type and *p*-type materials found in this study below 300K. Lower panel, the total thermoelectric figure of merit for an *n-p* couple made with two legs from the optimal *n*-type and *p*-type compounds.

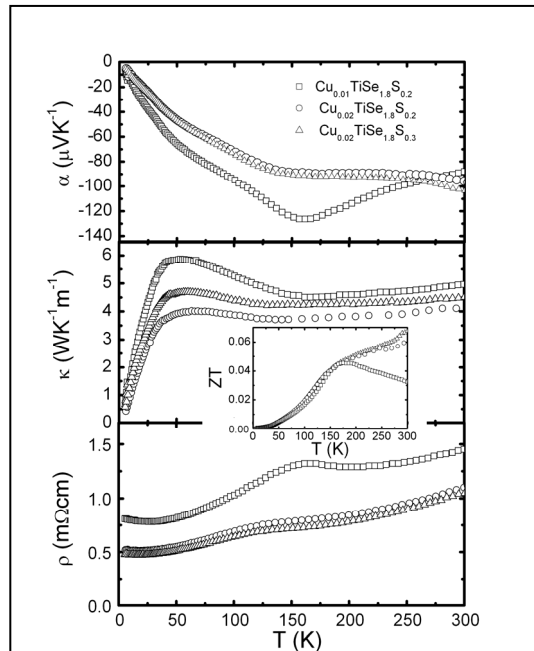


Fig. 5: Thermoelectric properties of the best $\text{Cu}_x\text{Ti}(\text{Se}_{1-y}\text{S}_y)_2$ materials. Upper: temperature dependence of the Seebeck coefficient; Middle: temperature dependence of the total thermal conductivity; Lower: temperature dependence of the electrical resistivity. Inset: temperature dependence of the thermoelectric figure of merit ZT .

Figure 4 shows the thermoelectric figure of merit values found for the best *n*- and *p*-type legs we have measured individually, and for the composite *n-p* couple. The lower panel indicates that the *n-p* couple is a useful overall thermoelectric system, though not better than others that have been reported, for the temperature region between about 300 and 100K.

Although this system has the advantage of ease of manufacture and chemical and electrical compatibility of *n*- and *p*-type legs, decreasing the thermal conductivities of the Bi-Sb alloys while maintaining their electrical resistivities will likely be the most productive research path to follow for improvement to be made in the performance of practical devices made from these materials.

$\text{Cu}_x\text{Ti}(\text{Se}_{1-y}\text{S}_y)_2$

There are two presently known physical effects that can yield high thermoelectric coefficients in conductive materials at ambient temperature and below. The first can be considered conventional – materials with very small band gaps are needed, and they should have several different electronic bands near the Fermi level, for both the valence band and the conduction band. This was the main focus of research on this project. The second, much more unconventional in origin, is related to magnetism, although the theory behind why this works has not yet been worked out; a high Seebeck coefficient appears in some conductive oxides, most famously cobalt oxides, when the electrical charge carriers also

carry localized magnetic moments during the charge transport process. During this research program we pursued several new materials in the magnetic materials class, in particular CoS_2 , and were able to obtain good thermoelectric properties, but that work was not completed. We did complete work on a system based on a

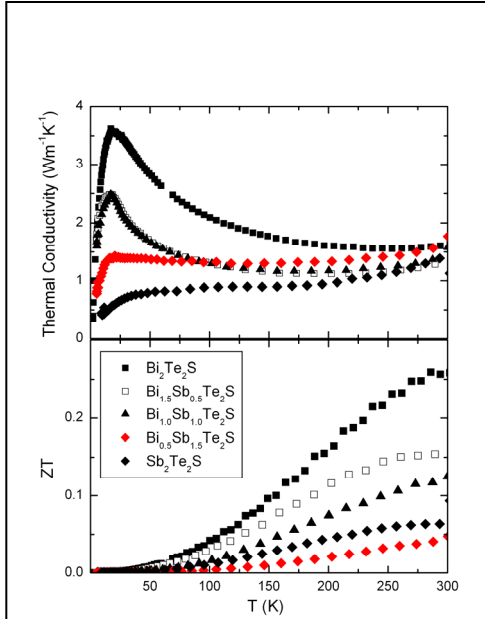


Fig. 6 : Upper panel: thermal conductivity for the $\text{Bi}_2\text{Te}_2\text{S}$ - $\text{Sb}_2\text{Te}_2\text{S}$ solid solution materials from 5 K to 300 K. Lower panel: ZT for the $\text{Bi}_2\text{Te}_2\text{S}$ - $\text{Sb}_2\text{Te}_2\text{S}$ solid solution materials from 5 K to 300 K.

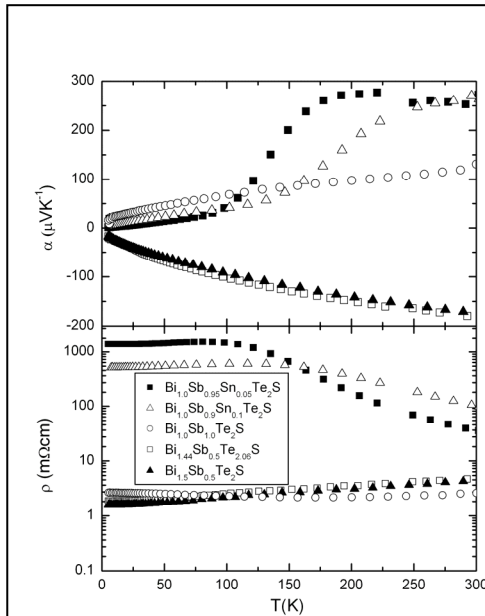


Fig. 7 The very high Seebeck coefficients for some of the materials in this system, coupled with the fact that semiconducting behavior can be obtained at low temperatures, suggests that further optimization of $\text{Bi}_2\text{Te}_2\text{S}$ -related materials will be possible. The thermal conductivities are extremely low.

newer kind of idea, that is, that materials with low temperature charge density waves (CDWs), where the charge transport and lattice are strongly coupled, might also display anomalously good thermoelectric properties. To test that idea we studied the system $\text{Cu}_x\text{Ti}(\text{Se}_{1-y}\text{S}_y)_2$, based on the small band gap semiconductor TiSe_2 . In TiSe_2 the small band gap is opened by the appearance of a charge density wave on cooling below 200K. We performed partial chemical substitution of S for Se to control the size of the band gap opened at the CDW transition. Simultaneously, we used Cu intercalation between the TiSe_2 layers to control the carrier concentration (Cu donates electrons to the conduction band) Our results show that while the thermoelectric properties are good compared to most materials, they are not nearly as good as those of Bi-Sb. Further work to look at the thermoelectric properties of charge density wave bearing materials as potential low temperature thermoelectrics would be of future interest.

$\text{Bi}_2\text{Te}_2\text{S}$ – $\text{Sb}_2\text{Te}_2\text{S}$

Returning to more conventional candidates for low temperature thermoelectrics, we completed a study of the low temperature properties of semiconducting materials structurally and chemically related to Bi_2Te_3 . In these materials the concept was to make the Bi_2Te_3 system less metallic at low temperatures and therefore increase the value of the low temperature thermoelectric coefficient. The hypothesis was that this could be accomplished through ordered

substitution of the more electropositive element S for Te in an ordered fashion between the Bi layers in the Bi_2Te_3 structure. In addition it was hypothesized that through partial substitution of Sb for Bi the low temperature properties might be improved. These kinds of studies have never before been performed on this type of variant of Bi_2Te_3 . The thermoelectric properties of the Tetradymite-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_2\text{S}$ solid solution ($0 \leq x \leq 2$) were determined for the temperature range 5 – 300 K. The properties of non-stoichiometric, Cl and Sn doped *n*- and *p*-type variants were determined as well. The Seebeck coefficients for these materials are very large, ranging from +270 to -170 μVK^{-1} , while the resistivities range from those of semimetals, 2 $\text{m}\Omega\text{cm}$, to semiconductors, > 1000 $\text{m}\Omega\text{cm}$. The achievement of true semiconducting behavior in a system related to Bi_2Te_3 is highly unusual, and possibly unique, and validates our hypothesis that the substitution of the more electropositive S in the crystal structure might result in such behavior. The thermal conductivities were low for most compositions, typically 1.5 $\text{Wm}^{-1}\text{K}^{-1}$, comparable to what is seen in Bi_2Te_3 . This low thermal conductivity is a very favorable characteristic of this system (see figure 6). Nominally undoped $\text{Bi}_2\text{Te}_2\text{S}$ shows the highest thermoelectric efficiency (ZT) amongst the tested materials, with a $\text{ZT} = 0.26$ at 300K. The ZT decreased to 0.04 at 100K making the material poor relative to Bi-Sb allows as a low temperature thermoelectric. A new compound, $\text{Sb}_2\text{Te}_2\text{S}$, was discovered in the course of this work and its

thermoelectric properties elucidated. It is concluded that our doping studies of Tetradymite-type materials

based on $\text{Bi}_2\text{Te}_2\text{S}$ show that the thermoelectric properties of this system are easily affected at small doping levels, illustrating the potential for improving their electrical resistivity, a necessary condition for improved thermoelectric efficiency. Further study into the purification of $\text{Sb}_2\text{Te}_2\text{S}$ would be needed in order to produce a detailed thermoelectric characterization of its properties. The exceptionally low thermal conductivities that these materials exhibit in combination with their high Seebeck coefficients may provide the basis for higher efficiency low temperature thermoelectric materials with further chemical optimization.

Ca-doped Bi_2Se_3

Bi_2Se_3 is one of the binary end-members of the $(\text{Bi,Sb})_2(\text{Te,Se})_3$ family of thermoelectric materials. Decades of work in the chemistry, physics, and processing of these materials has led to complex formulations of

compounds and microstructures optimized for use as thermoelectrics under various conditions. Due to the superiority of Bi_2Te_3 -based materials for these applications, Bi_2Se_3 , while well studied, has not been subject to the same degree of intensive research as has its heavier mass analog. One of the major issues for Bi_2Se_3 -based thermoelectrics has been the difficulty in making the material *p*-type. Unlike Bi_2Te_3 , which can simply be made *n*- or *p*-type through variation of the Bi:Te ratio, the defect chemistry in Bi_2Se_3 is dominated by charged selenium vacancies, which act as electron donors, resulting in *n*-type behavior for virtually all of the reported transport studies. *p*-type behavior for pure Bi_2Se_3 was reported in an early study, but never since. Modern studies have shown that *p*-type behavior is possible when beginning with an *n*-type host material in the $(\text{Bi}_{2-x}\text{Sb}_x)\text{Se}_3$ solid solution with $x = 0.4$, and then doping that composition with small amounts of Pb to create a quaternary *p*-type material.

This study was motivated by the desire to find a chemically less complex *p*-type Bi_2Se_3 -based material. Unlike the case for Bi_2Te_3 , where the chemical similarity of Bi and Te leads to antisite defects as the primary source of carrier doping in binary compounds, there is little tendency for Bi/Se mixing in Bi_2Se_3 , and the primary structural defect giving rise to electron doping is doubly charged selenium vacancies $\text{V}_{\text{Se}}^{\bullet\bullet}$: $\text{Se}_{\text{Se}} \rightarrow \text{V}_{\text{Se}}^{\bullet\bullet} + \text{Se}(\text{g}) + 2\text{e}'$. Ordinarily, one compensates for the presence of donors in this chemical family through doping with Pb on the Bi site, as Pb has one fewer electron than Bi. This substitution does

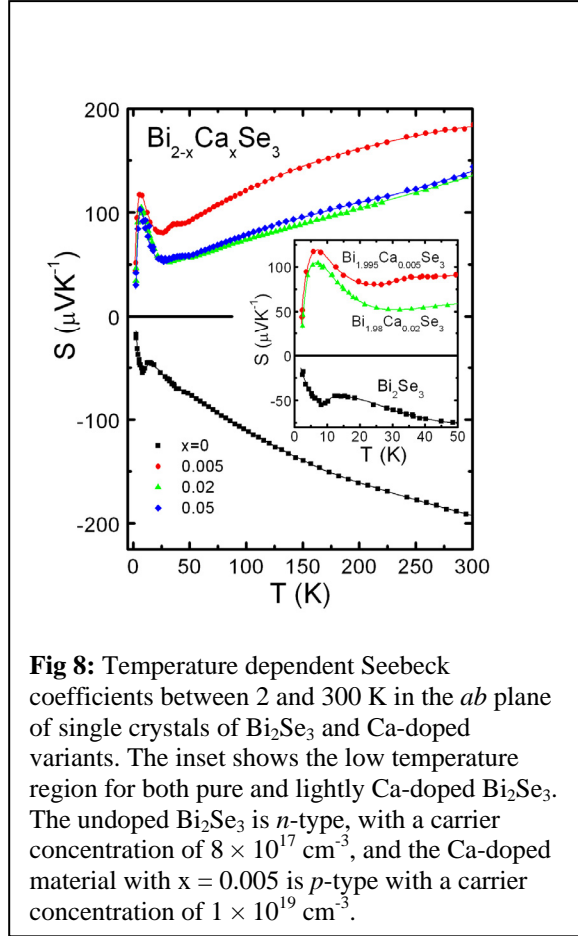


Fig 8: Temperature dependent Seebeck coefficients between 2 and 300 K in the *ab* plane of single crystals of Bi_2Se_3 and Ca-doped variants. The inset shows the low temperature region for both pure and lightly Ca-doped Bi_2Se_3 . The undoped Bi_2Se_3 is *n*-type, with a carrier concentration of $8 \times 10^{17} \text{ cm}^{-3}$, and the Ca-doped material with $x = 0.005$ is *p*-type with a carrier concentration of $1 \times 10^{19} \text{ cm}^{-3}$.

not, however, lead to the formation of *p*-type material for Bi_2Se_3 . We hypothesized that this is due to the fact that Pb in Bi_2Se_3 is ambipolar. This indicated that a more ionic substitution on the Bi site may be required for hole-doping of Bi_2Se_3 , suggesting the use of Ca substitution, with the defect reaction: $2\text{Ca} (\text{in } \text{Bi}_2\text{Se}_3) \rightarrow 2\text{Ca}_{\text{Bi}}' + 2\text{h}^\bullet$, with Ca substitution for Bi creating a negatively charged defect (Ca_{Bi}') that in turn generates holes (h^\bullet) to compensate the electrons created by the Se vacancies. The results support this scenario as a good representation of the defect chemistry in this compound.

The measurement of the low temperature properties of *p*-type and *n*-type Bi_2Se_3 , not previously known, revealed the presence of a dramatic anomaly in the low temperature thermoelectric coefficients. Representative data are shown in figure 8. The room temperature Seebeck coefficients are very large, in the range of $+200$ to $-200 \mu\text{VK}^{-1}$, making the materials of potential interest for room temperature applications, but most importantly relatively high thermoelectric coefficients are maintained down to low temperature, where a dramatic peak in the thermoelectric coefficient is observed. The low temperature Seebeck coefficient peaks of $-60 \mu\text{VK}^{-1}$ and $+120 \mu\text{VK}^{-1}$ for pure and doped Bi_2Se_3 at 7 K represent extremely high values when compared to other small band gap semiconductors at this low temperature. Although the origin of this very anomalous low temperature peak is not currently known, it is interesting that similarly anomalous low temperature peaks have been reported by some workers in $\text{Bi}_{1-x}\text{Sb}_x$ alloys, another material in the vicinity of a Dirac point. It is concluded that these materials are very promising for low temperature thermoelectrics. Future work on processing of the microstructure of *n*- and *p*-type Bi_2Se_3 to reduce the thermal conductivity to the $< 1 \text{ WK}^{-1}\text{m}^{-1}$ range typically

observed for polycrystalline materials in this family, if it can be performed while maintaining the power factors observed in the current work, promises the possibility of low temperature thermoelectric applications.

5. Personnel Supported:

Full time: postdoctoral fellows J.W.G. Bos (2006-7), Yew San Hor (2007-9). PI: one summer month each year. Undergraduate students Christopher Holmes-Parker, David Grauer and Clifford Engle summer research.